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**TRANSLATOR'S DECLARATION**

I, Kenji Ohdan, state:

that I am thoroughly familiar with both the Japanese and English languages; and

that the attached document represents a true English translation of the rough draft specification entitled "Outline of New Patent Application".

March 25, 2003      Kenji Ohdan  
Date                              Translator

## Outline of New Patent Application

### 1. Title of the invention (provisional):

Positive-working resist composition

### 2. Claims (proposed):

(1) A positive-working resist composition containing

(A) a resinous base ingredient which is a polymer containing (a-1) units having substitution for the hydrogen atoms of the phenolic hydroxyl groups or carboxyl groups by acid-dissociable groups and (a-2) hydroxystyrene units;

(B) a compound generating an acid by irradiation with a radiation;

(C) a divinyl ether compound crosslinkable with the component (A) by heating before exposure to light to form a positive-working resist film;

(D) an organic carboxylic acid excepting acid anhydrides which is free from nitrogen containing functional groups having basicity; and

(E) an organic amine.

(2) The positive-working resist composition described in Claim 1 in which the amounts of the components (C), (D) and (E) are, per 100 parts by weight of (A), 0.1 to 25 parts by weight of (C), 0.01 to 5 parts by weight of (D) and 0.01 to 1 part by weight of (E).

(3) The positive-working resist composition described in claim 1 or 2 in which the acid-dissociable group in the component (A) is at least one selected from lower alkoxyalkyl groups, tertiary alkoxy carbonyl groups, tertiary alkoxy carbonyl alkyl groups, tertiary alkyl groups and cyclic ether groups.

(4) The positive-working resist composition described in Claim 3 in which the component (A) comprises a mixture of (A1) a

polymer containing hydroxystyrene units which are substituted for the hydrogen atoms of the hydroxyl groups by alkoxyalkyl groups as the acid-dissociable groups and hydroxystyrene units; and (A2) a polymer containing hydroxystyrene units which are substituted for the hydrogen atoms of the hydroxyl groups by acid-dissociable groups selected from tertiary alkoxy carbonyl groups, tertiary alkyl groups and cyclic ether groups and hydroxystyrene units, the weight proportion of (A1) to (A2) being 2:8 to 9:1.

(5) The positive-working resist composition described in any one of claims 1 to 4 in which the component (D) is at least one selected from saturated or unsaturated aliphatic carboxylic acids, alicyclic carboxylic acids and aromatic carboxylic acids.

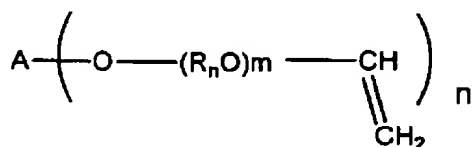
(6) The positive-working resist composition described in claim 5 in which the component (D) is at least one selected from maleic acid, malonic acid, dodecanoic acid or salicylic acid.

(7) The positive-working resist composition described in any one of claims 1 to 6 in which the component (E) is a secondary or tertiary aliphatic amine compound.

(8) The positive-working resist composition described in claim 7 in which the component (E) is a tertiary alkanol amine compound.

(9) The positive-working resist composition described in any one of claims 1 to 8 in which the component (C) is a divinyl ether compound expressed by the following general formula.

(I)



(A in the formula means an organic group having a valency of 2 to 5, R<sub>n</sub> means a lower alkyleneoxy group, m means an integer of 0 to 5 and n means an integer of 2 to 5)

(10) The positive-working resist composition described in claim 9 in which A in the general formula (I) means a chained or cyclic alkylene group having 1 to 6 carbon atoms, m is 0 and n is 2 or 3.

(11) A method for the formation of a patterned resist which comprises the steps of:  
coating the surface of a substrate with the positive-working resist composition of any one of claims 1 to 10 followed by drying to form a resist layer;  
exposing the resist layer pattern-wise through a mask pattern to light and subjecting the resist layer after exposure to light to a heat treatment after the exposure to light;  
subjecting the photoresist layer to a development treatment with an alkali to form a patterned resist; and  
heating the patterned resist to effect diminution of the pattern size to be smaller than that after the development by causing flow.

(12) The positive-working resist composition described in any one of claims 1 to 10 which is a positive-working resist composition which exhibits an amount of the size change per temperature of the formed patterned resist not exceeding 15 nm/°C.

### 3. Prior art technology and object of the present invention

In recent years, a great variety of chemical-amplification positive-working resists are proposed by virtue of the excellent pattern resolution and high sensitivity as compared with conventional non-chemical-amplification positive-working resists of types such as those formulated

with a naphthoquinone diazidosulfonic acid ester as the photosensitive agent and a novolak resin as the base resin and are already under practical applications in the process of the design rule 0.25 to 0.18  $\mu\text{m}$ . Nowadays, a density of integration of semiconductor devices tends to be higher and higher and mass production of LSIs with a design rule of about 0.15  $\mu\text{m}$  is proceeding at a high pitch.

Accordingly, as the resists for KrF excimer laser beams, various resist patterns such as line-and-space patterns, hole patterns and isolated patterns with fineness of 0.12 to 0.18  $\mu\text{m}$  are desired.

In Patent Kokai 6-148889, 6-230574, 8-62844 and 9-274320, inventions of so-called crosslink-type resists are proposed, in which chemical-amplification positive-working resists are admixed with a divinyl ether compound.

In these inventions, when such a resist is coated on a substrate and a resist film is formed by drying (pre-baking), the divinyl ether compound is thermally crosslinked with the resinous base ingredient and, then, by irradiation with light followed by a heat treatment (PEB), the acid generated from the acid-generating agent causes dissociation of the acid-dissociable groups and crosslinks formed in the pre-baking so that the contrast between the areas exposed to light and the areas unexposed to light against an alkaline developer solution to obtain a patterned resist with high resolution and excellent resistance against dry etching.

As the other side of possessing such an advantage, however, there is a problem of poor stability in the lapse of time. Stability in the lapse of time is a problem that resolution, profile of patterned resist, sensitivity and so on at preparation of a resist composition become deteriorated after lapse of several hours.

There is a process, which is called the thermal flow process in recent years when fineness of semiconductor devices is further increasing, wherein after a patterned resist is

formed via usual exposure to light, heating after exposure to light and lithography of an alkaline development, the patterned resist is subjected to flow by heating to form a patterned resist finer in the size of the resist pattern after development (Patent Kokai 2000-188250).

The thermal flow process has an advantage that the increase in fineness can be accomplished by using existing materials for resist so that increase in fineness can be performed without expensive investment. It is, however, necessary to strictly control the amount of pattern size of the resist at the temperature when a patterned resist after development is subjected to flow by heating to decrease the size of the patterned resist. Among the chemical-amplification resists having been proposed, there cannot be obtained one which is satisfactory and suitable for such a thermal flow process.

Accordingly, the object of the present invention is to provide a positive-working resist composition in which the above described problem of stability in the lapse of time is improved.

Thus, the object is to provide a positive-working resist composition which exhibits, while retaining the advantages including excellent pattern resolution and anti-etching resistance in the resist preparation as the merits of the aforementioned crosslink type, low susceptibility to the changes in time in the pattern profile and sensitivity.

Another object of the present invention is the object to provide a positive-working resist composition with a small dimensional change per unit temperature suitable for the thermal flow process.

#### 4. Means to accomplish the object

The object of the present invention can be accomplished by using, in a positive-working resist composition heretofore known containing (A) a resinous base ingredient consisting of

a polymer including (a-1) units in which the hydrogen atoms of phenolic hydroxyl groups or carboxyl groups are substituted by acid-dissociable groups and (a-2) hydroxystyrene units, (B) a compound capable of generating an acid by irradiation with a radiation and (C) a divinyl ether compound capable of crosslinking with the ingredient (A) by heating before light-exposure for the formation of a positive-working resist film, (D) an organic carboxylic acid excepting acid anhydrides, which is free from a nitrogen-containing functional group exhibiting basicity and (E) an organic amine in combination.

## 5. Description of constituting ingredients

Regarding the component (A)

The polymer containing the (a-1) units which are substituted for the hydrogen atoms of phenolic hydroxyl groups or carboxyl groups by acid-dissociable groups and (a-2) hydroxystyrene units is a polymer which is insoluble in an alkali due to solubility-reducing ability against alkali of the acid-dissociable groups and the solubility to aqueous alkaline solution thereof is increased in the areas exposed to light by interacting with the acid generated from the acid-generating agent.

Such polymers are known in wide variety as the resinous base ingredient for chemical-amplification positive-working resist or solubility reducing polymer and are not particularly limited.

Considering appropriate alkali-solubility, adhesivity to the substrate, heat-resistance and so on, it is necessary to be a polymer containing at least (a-1) a unit substituted for the hydrogen atom of phenolic hydroxyl group or carboxyl group by an acid-dissociable group and (a-2) a hydroxystyrene unit.

Although a great variety of acid-dissociable groups are already known in chemical-amplification positive-working resists and not particularly limitative, preferable are alkoxyalkyl groups, tertiary alkoxycarbonyl groups, tertiary

alkoxycarbonylalkyl groups, tertiary alkyl groups, cyclic ether groups and the like in consideration of their acid-dissociability and heat resistance and pattern profile.

The alkoxyalkyl group is exemplified by lower alkoxyalkyl groups such as 1-ethoxy-1-ethyl, 1-methoxy-1-propyl groups and the like.

The tertiary alkoxycarbonyl groups are exemplified by *tert*-butoxycarbonyl group, *tert*-amyloxycarbonyl group and the like.

The tertiary alkoxycarbonylalkyl groups are exemplified by *tert*-butoxycarbonylmethyl group, *tert*-butoxycarbonylethyl group, *tert*-amyloxycarbonylmethyl group, *tert*-amyloxycarbonylmethyl group and the like.

The tertiary alkyl groups are exemplified by *tert*-butyl group, *tert*-amyl group and the like.

The cyclic ether groups are exemplified by tetrahydropyranyl group, tetrahydrofuranyl group and the like.

More particularly, followings are given as examples.

(I) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% by mole of the hydroxyl groups thereof by at least one of acid-dissociable groups selected from lower alkoxyalkyl, tertiary alkoxycarbonyl, tertiary alkoxycarbonylalkyl and cyclic ether groups

(II) copolymer consisting of from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by acid-dissociable groups selected from tertiary alkyloxycarbonyl groups, tertiary alkyl groups and cyclic ether groups, from 10 to 49% of hydroxystyrene units for the hydrogen atoms of the hydroxyl groups by alkoxyalkyl groups and from 2 to 80% of hydroxystyrene units

(III) polymer containing (meth)acrylic acid ester units substituted for the hydrogen atoms of the carboxyl groups by acid-dissociable groups, hydroxystyrene units and styrene units

Particular examples of (I) include:



(I-1) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by 1-ethoxyethyl groups;

(I-2) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by *tert*-butoxy-carbonyl groups;

(I-3) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by *tert*-butoxy-carbonylmethyl groups;

(I-4) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by *tert*-butyl groups

(I-5) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by tetrahydropyranyl groups;

(I-6) polyhydroxystyrene substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by tetrafranyl groups; and the like.

Particular examples of (II) include:

(II-1) copolymer consisting of from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by *tert*-butoxycarbonyl groups, from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% of hydroxystyrene units;

(II-2) copolymer consisting of from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by *tert*-butyl groups, from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% of hydroxystyrene units;

(II-3) copolymer consisting of from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by tetrahydropyranyl groups, from 10 to 49% of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% of

hydroxystyrene units;  
and the like.

Particular examples of (III) include:  
polymers containing from 2 to 30% by moles of (meth)acrylic acid ester units substituted for the carboxyl hydrogen atoms by *tert*-butyl groups, from 40 to 80% by moles of hydroxystyrene units and from 10 to 40% by moles of styrene units; and  
polymers containing from 2 to 30% by moles of (meth)acrylic acid ester units substituted for the carboxyl hydrogen atoms by 1-ethylcyclohexyl groups, from 40 to 80% by moles of hydroxystyrene units and from 10 to 40% by moles of styrene units.

These polymers usually have a weight-average molecular weight from 2000 to 50000 or, preferably, from 5000 to 25000.

The molecular weight dispersion ( $M_w:M_n$ ) of these polymers is not particularly limited and usually in the range from 1.0 to 5.0 or, preferably, from 1.0 to 2.0 since resolution and heat-resistance can be improved by a smaller molecular weight distribution.

These respective polymers or copolymers can be used either singly or as a mixture of two kinds or more and, among them, particularly preferable in respect of high-resolution and excellent patterned resist profile are mixtures comprising (A1) a polymer containing hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by the acid-dissociable groups consisting of alkoxyalkyl groups and hydroxystyrene units such as (I-1) described above and (A2) a polymers containing hydroxystyrene units selected from the group of (I-4) and (I-5) substituted for the hydrogen atoms of the hydroxyl groups by acid-dissociable groups selected from tertiary alkyl groups and cyclic ether groups and hydroxystyrene units, the weight proportion of (A1) to (A2) being 1:9 to 9:1 weight proportion or, preferably, 4:6 to 9:1.

(B) Since many proposals have been made for the compound generating an acid by irradiation with a radiation, it is not particularly limitative and can be used optionally by selecting from these.

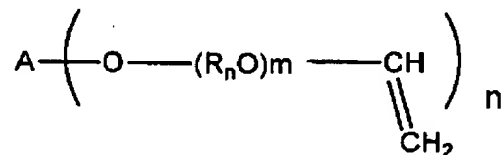
Preferable acid-generating compounds among them include diazomethane-based acid-generating compounds and onium salts with alkylsulfonic acid of which the alkyl group has 1 to 15 carbon atoms as the anion.

Regarding the component (C)

The divinyl ether compound crosslinkable with the component (A) by heating before exposure to light for forming a positive-working resist film is not particularly limitative provided that the divinyl ether compound is capable of thermally crosslinking with the resinous base ingredient at the so-called pre-baking when a resist film is formed by coating and drying.

A large number of such compounds are described in the prior art documents listed before as the prior art and can be freely used from among them.

Among these, in consideration of high-resolution and pattern profile of resist, the divinyl ether compound expressed by the following general formula (I) is preferable.  
(I)



(A in the formula means an organic group having di- to pentavalency,  $R_n$  means a lower alkyleneoxy group,  $m$  means an integer of 0 to 5 and  $n$  means an integer of 2 to 5).

This is described in [0029] to [0036] of Patent Kokai 9-274320.

Particularly, preferable is a compound in which A in the formula (I) is a divalent straightly linear or branched

alkylene group having 1 to 6 carbon atoms such as methylene, ethylene, propylene, butylene, pentylene, hexylene, cyclohexylene and heptylene groups or a trivalent organic group by removing a hydrogen atom from such an alkylene group, where m is 0 and n is 2 or 3.

Particular examples include:

ethyleneglycol divinyl ether,  
triethyleneglycol divinyl ether,  
1,3-butanediol divinyl ether,  
tetramethyleneglycol divinyl ether,  
neopentylglycol divinyl ether,  
trimethylolpropane trivinyl ether,  
trimethylolethane trivinyl ether,  
hexanediol divinyl ether,  
1,4-cyclohexanediol divinyl ether,  
tetraethyleneglycol divinyl ether,  
pentaerythritol divinyl ether,  
pentaerythritol trivinyl ether and the like.

Regarding the component (D)

The organic carboxylic acid excepting acid anhydrides which is free from a nitrogen-containing functional group having basicity is an organic carboxylic acid excepting a nitrogen-containing compound having a carboxyl group such as amino acid and a cyclic carboxylic acid anhydride.

The nitrogen-containing functional groups which are basic include basic functional groups such as amino group and imino group which greatly decrease acidity of the organic carboxylic acid and deteriorate the stability in the lapel of time if such basic functional groups are possessed. Acid anhydrides are not preferable since they cause defects after development due to their poor solubility in solvents for resist and low compatibility with the other ingredients.

Accordingly, the organic carboxylic acid in the present invention is that basically having at least one carboxyl

group, which may have a functional group, if not greatly affecting the acidity of the organic carboxylic acid, including, for example, acidic groups such as hydroxyl group and nitro group, and having excellent compatibility with solvents for resist and the other ingredients.

Particularly, saturated or unsaturated aliphatic carboxylic acids, alicyclic carboxylic acids, oxycarboxylic acids, alkoxycarboxylic acids, ketocarboxylic acids and aromatic carboxylic acids can be named though not particularly limited thereto.

The saturated aliphatic carboxylic acids are exemplified by mono- and polybasic carboxylic acids such as formic acid, acetic acid, propionic acid, dodecanoic acid, butyric acid, isobutyric acid, oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid. Examples of the unsaturated aliphatic carboxylic acids are exemplified by acrylic acid, crotonic acid, isocrotonic acid, 3-butenic acid, methacrylic acid, 4-pentenoic acid, propionic acid, 2-butyric acid, maleic acid, fumaric acid and acetylenecarboxylic acid. The alicyclic carboxylic acids are exemplified by 1,1-cyclohexane dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid and 1,1-cyclohexane diacetic acid.

The aromatic carboxylic acids are exemplified by aromatic carboxylic acids having a substituent group like hydroxyl or nitro group such as p-hydroxybenzoic acid, o-hydroxybenzoic acid, 2-hydroxy-3-nitrobenzoic acid, 2-nitrobenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, phthalic acid, terephthalic acid and isophthalic acid.

Among these carboxylic acids, at least one selected from saturated or unsaturated aliphatic carboxylic acids, alicyclic carboxylic acids and aromatic carboxylic acids such as maleic acid, malonic acid, dodecanoic acid, 1,1-cyclohexanedicar-

boxylic acid and salicylic acid are preferable because of their appropriate acidity and excellent compatibility with resist solvents.

Regarding the component (E)

The aliphatic amine is exemplified by secondary and tertiary aliphatic amines such as dimethylamine, trimethylamine, diethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-tert-butylamine, tripentylamine, diethanolamine, triethanolamine and tributanolamine.

Aromatic amines are exemplified by benzyl amine, aniline, N-methylaniline, N,N-dimethylaniline, o-methylaniline, m-methylaniline, p-methylaniline, N,N-diethylaniline, diphenylamine, di-p-tolylamine and the like.

Heterocyclic amines are exemplified by pyridine, o-methylpyridine, o-ethylpyridine, 2,3-dimethylpyridine, 4-ethyl-2-methylpyridine, 3-ethyl-4-methylpyridine and the like.

Among these, aliphatic amines or, in particular, alkanol amines such as diethanolamine, triethanolamine, tributanolamine and the like are preferable.

The feature of the present invention consists in the combined use of the components (C), (D) and (E). The problem of stability in lapse of time can be solved by using these together.

That is, the present inventors presumed that the problem of stability in time was caused by the vinyl groups in the component (C) with an assumption that polymerization of said groups during storage of the resist solution was responsible to the changes in the resolution, resist pattern profile and sensitivity leading to a discovery that combined use of the component (C) and component (E) would be effective in order to prevent polymerization of the vinyl groups in said groups.

In the method of the present invention described below,

by the combined use of the components (C), (D) and (E), in the step of thermal flow, crosslinking of the patterned resist proceeds and is imparted with high resistance against dry etching by increase of the molecular weight as well as the changes per unit temperature in the size of the patterned resist being low. The positive-working resist composition of the present invention can be expressed in term of the amount of changes and the value therefor should not exceed 15 nm/°C or, preferably, 10 nm/°C or, more preferably, 5 nm/°C.

Accordingly, effective compounding amounts of the components (C), (D) and (E) are, respectively, per 100 parts by weight of the component (A), from 0.1 to 25 parts by weight or, preferably, from 1 to 15 parts by weight of the component (C); from 0.01 to 5 parts by weight or, preferably, from 0.05 to 1 part by weight of the component (D); from 0.01 to 1 part by weight or, preferably, from 0.05 to 0.7 part by weight of the component (E).

Regarding the method for pattern formation

The method for pattern formation of the present invention is a method for formation of a pattern which comprises:

- (a) a step of coating the surface of a substrate with the positive-working resist composition of the present invention followed by drying to form a resist film;
- (b) a step of exposing the resist film to light through a mask pattern;
- (c) a step of subjecting the resist layer after exposure to light to a heat treatment after light-exposure;
- (d) a step of alkali development to form a resist pattern to form a patterned resist; followed by
- (e) a step of effecting flow of the resist pattern by heating thereby to render the size of the resist pattern smaller than the size after the development.

Each of these steps can be the step usually undertaken. In general, the method of spin coating is used for coating in

step (a) and the drying temperature is from 80 to 150 °C for 30 to 120 seconds. The heat treatment in step (e) is conducted on a hot plate at from 110 to 180 °C for 30 to 180 seconds.

## 6. Examples and Comparative Examples

Incidentally, the various properties of the positive-working resist compositions were determined in the following manner.

### (1) Sensitivity

A silicon wafer provided with an anti-reflection film of SWK-EX2 (a product by Tokyo Ohka Kogyo Co.) having a film thickness of 0.12  $\mu\text{m}$  was coated by using a spinner with the sample after lapse of 24 hours from resist preparation and the same was dried on a hot plate at 90 °C for 90 seconds to obtain a resist film having a film thickness of 0.5  $\mu\text{m}$ . This film was subjected to light-exposure with a KrF excimer laser by using a minifying projection light-exposure machine FPA-3000EX3 (manufactured by Canon Co.) with successive increments of dose each by 1  $\text{mJ}/\text{cm}^2$  followed by PEB (POST EXPOSURE BAKE) at 110 °C for 90 seconds and development at 23 °C taking 60 seconds with a 2.38% by weight aqueous solution of tetramethylammonium hydroxide followed by water rinse for 30 seconds and drying to determine the minimum light-exposure time taken as the sensitivity in the unit of  $\text{mJ}/\text{cm}^2$  (quantity of energy) by which the film thickness in the light-exposed areas after development was 0.

### (2) Profile of patterned resist

A 0.25  $\mu\text{m}$  line-and-space resist pattern obtained by the same procedure as in (1) above was evaluated for the profile thereof on a SEM (scanning electron microscope) photograph. Evaluation was made as A for those of rectangular form, B for tapered form and C for the form with round top and trailing



skirts.

(3) Pattern resolution

The critical resolution was examined on the line-and-space pattern obtained in the same procedure as in (1) above.

(4) Thermal flow behavior

The patterned resist of 0.25  $\mu\text{m}$  contact hole obtained in the same procedure as in (1) above was heated to be reduced down to 0.15  $\mu\text{m}$ . The thus formed 0.15  $\mu\text{m}$  resist pattern was evaluated for the flow rate (the amount of size change of the resist pattern per  $^{\circ}\text{C}$ ) expressed to give  $\odot$  for 5 nm/ $^{\circ}\text{C}$  or smaller,  $\bigcirc$  for exceeding 5 but not exceeding 15 nm/ $^{\circ}\text{C}$  and  $\times$  for exceeding 15 nm/ $^{\circ}\text{C}$ .

(5) Stability in time

Examination was carried out in the same manner as for (1) to (3) mentioned above excepting for the replacement of the sample to the sample after lapse of 24 days from preparation of the resist for (1') sensitivity, (2') resist pattern profile and (3') pattern resolution.

Example 1 (EV + t-boc).

A positive-working resist composition was prepared by dissolving, in 490 parts by weight of propyleneglycol monomethyl ether acetate,

(A1) 75 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups,

(A2) 25 parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 36% by moles of the hydroxyl

groups were substituted for the hydrogen atoms by *tert*-butoxycarbonyl groups,  
5 parts by weight of bis(cyclohexylsulfonyl) diazomethane,  
5 parts by weight of 1,4-cyclohexane dimethanol divinyl ether,  
0.1 part by weight of salicylic acid and  
0.2 part by weight of triethylamine  
followed by filtration thereof through a membrane filter of  
0.2  $\mu\text{m}$  pore diameter.

The results of the evaluation of this for the properties described above are shown in Table 1.

#### Example 2 (EV alone).

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, the component (A2) was not used and the component (A1) was taken in 100 parts by weight and then evaluation of the properties described above was made. The results thereof are shown in Table 1.

#### Example 3 (EV + THP).

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, replacement of the components (A1) and (A2) with the followings and was subjected to evaluation of the properties described above. The results are shown in Table 1.

(A1) parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups

(A3) parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 30% by moles of the hydroxyl groups were substituted for the hydrogen atoms by tetrahydropyranyl groups

Example 4 (EV + tert-butyl).

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, the replacement of the components (A1) and (A2) with the followings and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

(A1) parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups

(A3) parts by weight of a polyhydroxystyrene having a weight-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 30% by moles of the hydroxyl groups were substituted for the hydrogen atoms by tert-butyl groups

Example 5 (HAER).

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, the replacement of the components (A1) and (A2) with the followings and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

60 parts by weight of a copolymer having a weight-average molecular weight of 10000 and consisting of 65% by moles of hydroxystyrene, 20% by moles of styrene and 15% by moles of tert-butyl acrylate

40 parts by weight of a copolymer having a weight-average molecular weight of 10000 and consisting of 75% by moles of hydroxystyrene, 20% by moles of styrene and 5% by moles of tert-butyl acrylate.

Comparative Example 1.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, omission

of salicylic acid and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

#### Comparative Example 2.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, omission of triethylamine and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

#### Comparative Example 3.

A positive-working resist composition was prepared in the same manner as in Example 2 excepting, in Example 2, omission of salicylic acid and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

#### Comparative Example 4.

A positive-working resist composition was prepared in the same manner as in Example 2 excepting, in Example 2, omission of triethylamine and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

#### Comparative Example 5.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, omission of 1,4-cyclohexane dimethanol divinyl ether and was subjected to evaluation of the properties described above. The results are summarized in Table 1.

Table 1

Example/ Compara- tive Example	Sensitivity (mJ/cm <sup>2</sup> )		Profile of patterned resist		Resolu- tion (μm)		Resist- ance against etching
	(1)	(1')	(2)	(2')	(3)	(3')	
Example 1	45	45	rectangular	rectangular	0.19	0.19	⊙
Example 2	47	47	rectangular	rectangular	0.18	0.18	○
Example 3	45	45	rectangular	rectangular	0.19	0.19	⊙
Example 4	45	45	rectangular	rectangular	0.20	0.20	⊙
Example 5	25	25	rectangular	rectangular	0.19	0.19	⊙
Comparative Example 1	30	35	inversly taperd	inversly taperd	0.24	0.24	○
Comparative Example 2	20	33	trapezoidal	trapezoidal	0.25	0.25	○
Comparative Example 3	20	25	inversly taperd	inversly taperd	0.23	0.23	×
Comparative Example 4	18	28	trapezoidal	trapezoidal	0.23	0.23	×
Comparative Example 5	35	35	rectangular	rectangular	0.20	0.21	△



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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of : Confirmation No. 8121  
Kazuyuki NITTA et al. : Docket No. 2001-1143A  
Serial No. 09/928,430 : Group Art Unit 1752  
Filed August 14, 2001 : Examiner S. Lee

POSITIVE-WORKING PHOTORESIST  
COMPOSITION AND RESIST  
PATTERNING METHOD USING SAME

DECLARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Nobue Kanaka, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;  
that I am presently engaged as a translator in these languages;  
that the attached document represents a true English translation of the Japanese Priority  
Application No. 2000-264529, filed August 31, 2000.

I further declare that all statements made herein of my own knowledge are true and that  
all statements on information and belief are believed to be true; and further that these  
statements were made with the knowledge that willful false statements and the like so made are  
punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United  
States Code, and that such willful false statements may jeopardize the validity of the application  
or any patent issuing thereon.

Signed this *28th* day of *August*, 2003.

*Nobue Kanaka*

Translator

PATENT OFFICE  
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of  
the following application as filed with this office.

Date of Application: August 31, 2000  
Application Number: Patent Application No. 2000-264529  
Applicant: TOKYO OHKA KOGYO CO., LTD.

May 31, 2001

Commissioner,  
Patent Office OIKAWA, Kozo (Seal)

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[Name of document] Specification

[Title of the invention] Positive-working resist composition and method for the formation of patterned resist using same

[The claims]

[Claim 1] A positive-working resist composition containing

(A) a resinous base ingredient consisting of at least one kind of hydroxystyrene-based copolymers of which at least a part of the phenolic hydroxyl groups or carboxyl groups are substituted for the hydrogen atoms thereof by acid-dissociable groups;

(B) a compound generating an acid by irradiation with a radiation;

(C) a divinyl ether compound having crosslinkability;

(D) an organic carboxylic acid consisting of atoms of carbon, oxygen and hydrogen alone; and

(E) an organic amine.

[Claim 2] The positive-working resist composition described in Claim 1 which contains, per 100 parts by mass of (A), 0.1 to 25 parts by mass of (C), 0.01 to 5 parts by mass of (D) and 0.01 to 1 part by mass of (E).

[Claim 3] The positive-working resist composition described in claim 1 or 2 in which the acid-dissociable group in the component (A) is at least one kind selected from lower alkoxyalkyl groups, tertiary alkoxycarbonyl groups, tertiary alkoxycarbonylalkyl groups, tertiary alkyl groups and cyclic ether groups.

[Claim 4] The positive-working resist composition described in Claim 1, 2 or 3 in which the component (A) comprises a mixture of (a<sub>1</sub>) a polyhydroxystyrene of which a part of the phenolic hydroxyl groups are substituted for the hydrogen atoms thereof by at least one kind of acid-dissociable groups selected from alkoxyalkyl groups; and (a<sub>2</sub>) a polyhydroxystyrene of which a part of the phenolic hydroxyl groups are substituted for the hydrogen atoms thereof by at least one kind of acid-dissociable groups selected from tertiary alkoxycarbonyl groups, tertiary alkyl groups and cyclic ether groups.

[Claim 5] The positive-working resist composition described in claim 4 in which the mixing proportion of (a<sub>1</sub>) to (a<sub>2</sub>) is 2:8 to

9:1 in mass proportion.

[Claim 6] The positive-working resist composition described in any one of claims 1 to 5 in which the component (C) is a divinyl ether compound represented by the general formula



(X in the formula is a residue removing at least two hydroxyl groups from a hydrocarbonyl group having 2 to 4 hydroxyl groups which may interrupted by an oxygen atom, and n is an integer of 2 to 4).

[Claim 7] The positive-working resist composition described in claim 6 in which X in the general formula is a straightly linear or branched alkylene group having 1 to 8 carbon atoms or an alkylene group having 6 to 8 carbon atoms with alicyclic group having 4 to 6 carbon atoms.

[Claim 8] The positive-working resist composition described in any one of claims 1 to 7 in which the component (D) is at least one kind selected from saturated or unsaturated aliphatic carboxylic acids with or without substitution by hydroxyl groups, alicyclic carboxylic acids and aromatic carboxylic acids.

[Claim 9] The positive-working resist composition described in claim 8 in which the saturated or unsaturated aliphatic carboxylic acid, alicyclic carboxylic acid or aromatic carboxylic acid is maleic acid, malonic acid, dodecanoic acid or salicylic acid.

[Claim 10] The positive-working resist composition described in any one of claims 1 to 9 in which the component (E) is a secondary or tertiary aliphatic amine.

[Claim 11] The positive-working resist composition described in claim 10 in which the secondary or tertiary aliphatic amine is a dialkanol amine or trialkanol amine.

[Claim 12] A method for the formation of a patterned resist which comprises the steps of: coating a substrate with the positive-working resist composition of any one of claims 1 to 11 followed by drying to form a resist layer; exposing the aforementioned resist layer through a mask pattern to light; subjecting the resist layer after exposure to light to a heat

treatment; then, developing the resist layer with an alkali to form a patterned resist; and heating the patterned resist to effect diminution of size of the patterned resist to be smaller than that immediately after the development by causing flow.

[Claim 13] The method for the formation of a patterned resist described in claim 12 in which the patterned resist having an amount of size change per temperature not exceeding 15 nm/°C is formed.

[Detailed description of the invention]

[0001]

[Technical Field to which the Invention belongs]

The present invention relates to a positive-working resist composition having good pattern resolution and stability in the lapse of time and capable of giving a patterned resist with controlled little amount of size changes per temperature by the thermal flow process as well as to a method for the formation of a patterned resist by using the same.

[0002]

[Prior art]

Recently, a great variety of chemical-amplification positive-working resists are proposed by virtue of the excellent pattern resolution and high sensitivity as compared with conventional non-chemical-amplification positive-working resists such as those formulated with a naphthoquinone diazidosulfonic acid ester as the photosensitive agent and a novolak resin as the base resin and are already under practical applications in the process of the design rule 0.25 to 0.18  $\mu\text{m}$ .

On the other hand, in respect of semiconductor devices, a density of integration tends to be higher and higher and, along with proceeding of mass production of LSIs with a design rule of about 0.15  $\mu\text{m}$ , as the resists for KrF excimer, various patterned resists such as line-and-space patterns, hole patterns and isolated patterns with fineness of 0.12 to 0.18  $\mu\text{m}$  are desired.

[0003]

By the way, a so-called crosslink-type resists are known,

in which chemical-amplification positive-working resists are admixed with a divinyl ether compound (publications of Patent Kokai 6-148889, 6-230574, 8-62844 and 9-274320).

[0004]

When such a resist is coated on a substrate and a resist film is formed by drying (pre-baking), the divinyl ether compound is thermally crosslinked with the resinous base ingredient and, then, by exposure to light followed by a heat treatment, the acid generated from the acid-generating agent causes dissociation of the acid-dissociable groups and crosslinks formed in the pre-baking so that the contrast between the areas exposed to light and the areas unexposed to light against an alkaline developer solution to give a patterned resist with high resolution and excellent resistance against dry etching.

[0005]

Such a chemical-amplification positive-working resist of the crosslinked type, however, has a defect that the pattern resolution, profile of the patterned resist, sensitivity and the like at preparation of the resist composition become deteriorated after lapse of several hours to several days.

[0006]

Further, recently, the so-called thermal flow process is proposed, which is a process wherein after a patterned resist is formed via usual exposure to light, heating after exposure to light and lithographic process of a development, the patterned resist is subjected to flow by heating to form a patterned resist finer in the size of the patterned resist immediately after development (publication of Patent Kokai 2000-188250).

[0007]

This thermal flow process has an advantage that the increase in fineness can be accomplished by using existing materials for resist so that it meets a demand for increase in fineness can be performed without expensive investment but has a problem of difficulty in control of the amount of change of pattern size of the resist at the temperature when a patterned

resist after development is subjected to flow by heating to decrease the size of the patterned resist so that it is the status quo that no chemical-amplification resist has been obtained suitable therefor.

[0008]

[Problem to be solved by the Invention]

The present invention, under these circumstances, has been accomplished with an object to provide a positive-working resist composition having good stability in the lapse of time and capable of giving a patterned resist having excellent pattern resolution and resistance against etching with a small amount of dimensional change per unit temperature by the thermal flow process.

[0009]

[Means for solving Problem]

The inventors have continued extensive investigations regarding a chemical-amplification positive-working resist, as a result, find that, by admixing a divinyl ether compound capable of crosslinking, an organic carboxylic acid consisting of specific atoms and an organic amine with a specific resinous base ingredient, a positive-working resist composition having good pattern resolution and stability in the lapse of time and capable of giving a patterned resist having excellent resistance against etching with a small amount of dimensional change per unit temperature by the thermal flow process, leading to the establishment of the present invention based thereon.

[0010]

Namely, the present invention provides a positive-working resist composition containing (A) a resinous base ingredient consisting of at least one kind of hydroxystyrene-based copolymers of which at least a part of the phenolic hydroxyl groups or carboxyl groups are substituted for the hydrogen atoms thereof by acid-dissociable groups, (B) a compound generating an acid by irradiation with a radiation, (C) a divinyl ether compound having crosslinkability, (D) an organic carboxylic acid consisting of atoms of carbon, oxygen and

hydrogen alone and (E) an organic amine as well as a method for the formation of a patterned resist which comprises the steps of: coating a substrate with the aforementioned positive-working resist composition followed by drying to form a resist layer; exposing the aforementioned resist layer through a mask pattern to light; subjecting the resist layer after exposure to light to a heat treatment; then, developing the resist layer with an alkali to form a patterned resist; and heating the patterned resist to effect diminution of size of the patterned resist to be smaller than that immediately after the development by causing flow.

[0011]

[Embodiment of the Invention]

The inventive chemical-amplification positive-working resist contains (A) a resinous base ingredient consisting of at least one kind of hydroxystyrene-based copolymers of which at least a part of the phenolic hydroxyl groups or carboxyl groups are substituted for the hydrogen atoms thereof by acid-dissociable groups.

[0012]

The resinous base ingredient as the component (A) is insoluble in an alkali before the light exposure due to solubility-reducing ability against alkali of the acid-dissociable groups and, after light exposure, the solubility to aqueous alkaline solution thereof is increased in the areas exposed to light by interacting with the acid generated from the acid-generating agent to release the acid-dissociable groups. While the acid-dissociable groups are not particularly limitative, preferable are lower alkoxyalkyl groups, tertiary alkoxy carbonyl groups, tertiary alkoxy carbonyl alkyl groups, tertiary alkyl groups and cyclic ether groups in consideration of their acid-dissociability and heat resistance and pattern profile.

[0013]

The lower alkoxyalkyl group is exemplified by 1-ethoxy-1-ethyl group, 1-methoxy-1-propyl groups and the like, the tertiary alkoxy carbonyl group is exemplified by tert-

butoxycarbonyl group, *tert*-amyloxycarbonyl group and the like, the tertiary alkoxycarbonylalkyl group is exemplified by *tert*-butoxycarbonylmethyl group, *tert*-butoxycarbonylethyl group, *tert*-amyloxycarbonylmethyl group, *tert*-amyloxycarbonylethyl group and the like, the tertiary alkyl group is exemplified by *tert*-butyl group, *tert*-amyl group and the like, the cyclic ether group is exemplified by tetrahydropyranyl group, tetrahydrofuranlyl group and the like.

[0014]

Thus, the resinous base ingredient (A) is exemplified by polyhydroxystyrenes and the like substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by at least one of acid-dissociable groups selected from lower alkoxyalkyl, tertiary alkoxycarbonyl, tertiary alkoxycarbonylalkyl and cyclic ether groups. Preferable among these are polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by 1-ethoxyethyl groups, polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by *tert*-butoxycarbonyl groups, polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by *tert*-butoxycarbonylmethyl groups, polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by *tert*-butyl groups and polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups thereof by tetrahydropyranyl groups.

[0015]

Also nominated are copolymers consisting of from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by acid-dissociable groups selected from tertiary alkyloxycarbonyl groups, tertiary alkyl groups and cyclic ether groups, from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by alkoxyalkyl groups and from 2 to 80% by moles of hydroxystyrene units. These can be exemplified by copolymers consisting of from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the



hydroxyl groups by *tert*-butoxycarbonyl groups, from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% by moles of hydroxystyrene units; copolymers consisting of from 10 to 49% by moles of hydroxy-styrene units substituted for the hydrogen atoms of the hydroxyl groups by *tert*-butyl groups, from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% by moles of hydroxystyrene units; copolymers consisting of from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by tetrahydropyranyl groups, from 10 to 49% by moles of hydroxystyrene units substituted for the hydrogen atoms of the hydroxyl groups by 1-ethoxyethyl groups and from 2 to 80% by moles of hydroxystyrene units and the like.

[0016]

Further, example of a polymer containing (meth)acrylic acid ester units substituted for the hydrogen atoms of the carboxyl groups by acid-dissociable groups, hydroxystyrene units and styrene units include: polymers containing from 2 to 30% by moles of (meth)acrylic acid ester units substituted for the carboxyl hydrogen atoms by *tert*-butyl groups, from 40 to 80% by moles of hydroxystyrene units and from 10 to 40% by moles of styrene units; polymers containing from 2 to 30% by moles of (meth)acrylic acid ester units substituted for the carboxyl hydrogen atoms by 1-ethylcyclohexyl groups, from 40 to 80% by moles of hydroxystyrene units and from 10 to 40% by moles of styrene units and the like. These polymers or copolymers usually have a mass-average molecular weight from 2000 to 50000 or, preferably, from 5000 to 25000. Besides, the molecular weight dispersion ( $M_w/M_n$ ) is usually in the range from 1.0 to 5.0 or, preferably, from 1.0 to 2.0.

[0017]

These polymers or copolymers can be used either singly or as a combination of two kinds or more. In such a case, preferable is a mixture of ( $a_1$ ) a polyhydroxystyrene substituted for the hydrogen atoms of a part of the phenolic hydroxyl

groups by at least a kind of the acid-dissociable groups selected from alkoxyalkyl groups and (a<sub>2</sub>) a polyhydroxystyrene substituted for the hydrogen atoms of a part of the hydroxyl groups by at least a kind of the acid-dissociable groups selected from tertiary alkoxy carbonyl groups, tertiary alkyl groups and cyclic ether groups, the mixing proportion of (a<sub>1</sub>): (a<sub>2</sub>) being 2:8 to 9:1 or, particularly, from 4:6 to 9:1 in mass proportion.

[0018]

Examples thereof include mixtures of polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups by 1-ethoxyethyl groups with polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups by tert-butoxycarbonyl groups, polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups by tert-butyl groups or polyhydroxystyrenes substituted for the hydrogen atoms of 10 to 60% of the hydroxyl groups by tetrahydropyranyl groups.

[0019]

In the inventive chemical-amplification positive-working resist composition, (B) a compound generating an acid by irradiation with a radiation (hereinafter referred to as an acid-generating agent) can be used as selected from the known acid-generating agents used in the conventional chemical-amplification photoresists, among them particularly preferable are diazomethane-based acid-generating agents and onium salts with fluoroalkylsulfonic acid ions having 1 to 15 carbon atoms.

[0020]

Examples of the diazomethanes include bis(p-toluene-sulfonyl)diazomethane, bis(1,1-dimethylethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane and bis(2,4-dimethylphenylsulfonyl)diazomethane.

Besides, examples of the onium salts include diphenyliodonium trifluoromethanesulfonate and nonafluorobutanesulfonate, bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate and nonafluorobutanesulfonate, triphenylsulfonium trifluoromethanesulfonate and nonafluorobutanesulfonate and

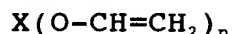
tri(4-methylphenyl)sulfonium trifluoromethanesulfonate and nonafluorobutanesulfonate, of which diphenyliodonium bis(4-tert-butylphenyl)iodonium trifluoromethanesulfonate and nonafluorobutanesulfonate are particularly preferable.

[0021]

The acid-generating agents as the component (B) can be used either singly or as a combination of two kinds or more. The content thereof is usually selected in the range from 1 to 20 parts by mass per 100 parts by mass of the component (A) aforementioned. When the acid-generating agent is smaller than 1 part by mass, an image can hardly be formed while, when larger than 20 parts by mass, a uniform solution cannot be obtained to decrease storage stability.

[0022]

In the invention, it is necessary to formulate a divinyl ether compound having crosslinkability as the component (C), which is not particularly limitative provided that it is capable of thermally crosslinking with the resinous base ingredient when a resist film is formed by coating on the resist substrate and drying. Particularly preferable as the component (C) is a divinyl ether compound represented by the general formula



(X in the formula is a residue removing at least two hydroxyl groups from a hydrocarbonyl group having 2 to 4 hydroxyl groups which may interrupted by an oxygen atom, and n is an integer of 2 to 4).

[0023]

The X is a straightly linear or branched alkylene group having 1 to 8 carbon atoms or an alkylene group having 6 to 8 carbon atoms with an alicyclic group having 4 to 6 carbon atoms. These include, for example, ethyleneglycol divinyl ether, triethyleneglycol divinyl ether, 1,3-butanediol divinyl ether, tetramethyleneglycol divinyl ether, neopentylglycol divinyl ether, trimethylolpropane trivinyl ether, trimethylol-ethane trivinyl ether, hexanediol divinyl ether, 1,4-cyclohexanediol divinyl ether, tetraethyleneglycol divinyl

ether, pentaerythritol divinyl ether, pentaerythritol trivinyl ether, cyclohexane dimethanol divinyl ether and the like.

Among these, divinyl ethers of alkylene glycol having an alicyclic group such as cyclohexane dimethanol divinyl ether are particularly preferable.

[0024]

The divinyl ether compound having crosslinkability as the component (C) is usually selected in the range from 0.1 to 25 parts by mass or, preferably, from 1 to 15 parts by mass per 100 parts by mass of the component (A). These can be used either singly or as a mixture of two kinds or more.

[0025]

Besides, as the component (D) in the invention, an organic carboxylic acid consisting of atoms of carbon, oxygen and hydrogen alone is used, which should be free from a nitrogen-containing substituent group and there is used at least one kind selected from saturated or unsaturated aliphatic carboxylic acids which may be unsubstituted or substituted by a hydroxyl group, alicyclic carboxylic acids and aromatic carboxylic acids.

[0026]

Examples of the saturated alicyclic carboxylic acids include, for example, formic acid, acetic acid, propionic acid, dodecanoic acid, butyric acid, isobutyric acid, oxalic acid, malonic acid, succinic acid, glutaric acid and adipic acid; examples of the unsaturated aliphatic carboxylic acids include, for example, acrylic acid, crotonic acid, isocrotonic acid, 3-butenic acid, methacrylic acid, 4-pentenoic acid, propionic acid, 2-butenic acid, maleic acid, fumaric acid and acetylenecarboxylic acid; examples of the alicyclic carboxylic acids include, for example, 1,1-cyclohexane dicarboxylic acid, 1,2-cyclohexane dicarboxylic acid, 1,3-cyclohexane dicarboxylic acid, 1,4-cyclohexane dicarboxylic acid and 1,1-cyclohexyl diacetic acid; and examples of the aromatic carboxylic acids include, for example, p-hydroxybenzoic acid, o-hydroxybenzoic acid, 2-hydroxy-3-nitrobenzoic acid, 2-nitrobenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-

dihydroxybenzoic acid, 3,4-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, phthalic acid, terephthalic acid and isophthalic acid. Among these, maleic acid, malonic acid, dodecanoic acid and salicylic acid are preferable.

[0027]

The organic carboxylic acid as the component (D) is used in the range from 0.01 to 5 parts by mass or, preferably, from 0.05 to 1 part by mass per 100 parts by mass of the component (A) aforementioned. These can be used either singly or as a mixture of two kinds or more.

[0028]

As the organic amine as the component (E) in the invention, a secondary or tertiary aliphatic amine is preferable. These include, for example, dimethylamine, trimethylamine, diethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-tert-butylamine, tripropylamine, diethanolamine, triethanolamine, tributanolamine and the like. Among them, dialkanol amines and trialkanol amines such as diethanolamine, triethanolamine and tributanolamine are preferable.

[0029]

The organic amine as the component (E) is usually used in the range from 0.01 to 1 part by mass or, preferably, from 0.05 to 0.7 part by mass per 100 parts by mass of the component (A). These can be used either singly or as a combination of two kinds or more.

[0030]

The inventive positive-working resist composition is, when used, preferably used as a solution prepared by dissolving each of the components in a solvent. Examples of the solvents used herein include ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptanone, polyhydric alcohols and derivatives thereof such as ethyleneglycol, ethyleneglycol monoacetate, diethyleneglycol, diethyleneglycol monoacetate, propyleneglycol, propyleneglycol monoacetate, dipropyleneglycol and dipropyleneglycol monoacetate as well as monomethyl, monoethyl, monopropyl, monobutyl and monophenyl

ethers thereof, cyclic ethers such as dioxane and esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate and ethyl ethoxypropionate. These can be used either singly or as a mixture of two kinds or more.

[0031]

It is optional that the inventive composition is further admixed with additives conventionally used having miscibility therewith such as auxiliary resins to improve the properties of the resist layer, plasticizers, stabilizers, coloring agents, surface active agents and the like.

[0032]

In the next, the formation of the inventive patterned resist is conducted by using a known method for the formation of a patterned resist. Such a method for the formation comprises the steps of:  
coating the solution of the resist composition on a substrate such as a silicon wafer or substrate provided with an anti-reflection coating film according to need by using a spinner followed by drying to form a resist layer thereon; irradiating same with KrF excimer laser beams through a desired mask pattern by means of an apparatus for exposure to KrF to form a latent image followed by a heat treatment; subjecting same to the development treatment with an aqueous alkaline developer solution such as a 0.1 to 10% by mass aqueous solution of tetramethylammonium hydroxide; and heating this patterned resist to cause diminishing of the patterned resist size by flow smaller than the size of that immediately after the development.

To conduct the invention suitably, when the inventive positive-working resist composition is coated on a substrate and dried to provide a resist layer, the drying is conducted at 80 to 150 °C for 30 to 120 seconds.

[0033]

Nextly, the patterned resist after exposure to light is subjected to post-heating on a hot plate at 90 to 150 °C for 30 to 120 seconds. Further, to diminish the size of the patterned

resist smaller than that immediately after development, heating is conducted on a hot plate at a temperature from 110 to 180 °C for 130 to 180 seconds.

[0034]

The inventive positive-working resist composition contains a divinyl ether compound having crosslinkability as the component (C), which causes decreasing of the stability in the lapse of time. In the invention, the decrease of the change in the lapse of time is suppressed by the combined use of the components (D) and (E). Then, in the step of the thermal flow, a crosslinking of the patterned resist proceeds to increase the molecular weight so that high resistance against dry etching is obtained and the amount of dimensional changes per unit temperature can be controlled low. These dimensional changes per unit temperature should not exceed 15 nm/°C or, preferably, 5 nm/°C.

[0035]

[Effect of the invention]

According to the invention, obtained is a positive-working resist composition having good stability in the lapse of time and capable of giving a patterned resist having excellent pattern resolution with a small amount of dimensional change per unit temperature by the thermal flow process.

[0036]

[Example]

In the following, the invention is described in more detail by way of examples but never limited by these examples.

[0037]

Incidentally, the properties of the positive-working resist compositions were determined in the following manner.

(1) Sensitivity:

A silicon wafer provided with an anti-reflection film of SWK-EX2 (a tradenames, produced by Tokyo Ohka Kogyo Co.) having a film thickness of 0.12  $\mu\text{m}$  was coated by using a spinner with the sample after lapse of 24 hours from resist preparation and the same was dried on a hot plate at 90 °C for 90 seconds to obtain a resist film having a film thickness of 0.5  $\mu\text{m}$ . This

film was subjected to light-exposure with a KrF excimer laser beam by using a minifying projection light-exposure machine FPA-3000EX3 (manufactured by Canon Co.) with successive increments of dose each by  $1 \text{ mJ/cm}^2$  followed by heat treatment at  $110^\circ\text{C}$  for 90 seconds and development at  $23^\circ\text{C}$  taking 60 seconds with a 2.38% by mass aqueous solution of tetramethyl-ammonium hydroxide followed by water rinse for 30 seconds and drying to determine the minimum light-exposure time taken as the sensitivity in the unit of  $\text{mJ/cm}^2$  by which the film thickness in the light-exposed areas after development was 0.

[0036]

(2) Profile of patterned resist:

The profile of a  $0.25 \mu\text{m}$  line-and-space patterned resist obtained by the same procedure as in (1) above was evaluated on a SEM (scanning electron microscope) photograph. Evaluation was made as A for those of rectangular form, B for tapered form and C for the form with round top and trailing skirts.

[0039]

(3) Pattern resolution:

The critical resolution was examined on the line-and-space pattern obtained in the same procedure as in (1) above.

[0040]

(4) Thermal flow characteristics:

The patterned resist of  $0.25 \mu\text{m}$  contact hole obtained in the same procedure as in (1) above was heated to be reduced down to  $0.15 \mu\text{m}$ , which was evaluated for the flow rate (the amount of size change of the patterned resist per  $^\circ\text{C}$ ) expressed to give  $\odot$  for  $5 \text{ nm}/^\circ\text{C}$  or smaller,  $\bigcirc$  for exceeding 5 but not exceeding  $15 \text{ nm}/^\circ\text{C}$  and  $\times$  for exceeding  $15 \text{ nm}/^\circ\text{C}$ .

[0041]

(5) Stability in lapse of time:

Examination was carried out in the same manner as for the procedures (1) to (3) mentioned above excepting for the replacement of the sample to the sample after lapse of 24 days from preparation of the resist.

[0042]

Example 1.



A positive-working resist composition was prepared by dissolving, in 490 parts by mass of propyleneglycol monomethyl ether acetate, a mixture of 75 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, and 25 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 36% by moles of the hydroxyl groups were substituted for the hydrogen atoms by *tert*-butoxycarbonyl groups, with admixture of 5 parts by mass of bis(cyclohexylsulfonyl) diazomethane, 5 parts by mass of 1,4-cyclohexane dimethanol divinyl ether, 0.1 part by mass of salicylic acid and 0.2 part by mass of triethylamine followed by filtration thereof through a membrane filter of 0.2  $\mu\text{m}$  pore diameter. Characteristics thereof are shown in Table 1.

[0043]

Example 2.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, the polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 36% by moles of the hydroxyl groups were substituted for the hydrogen atoms by *tert*-butoxycarbonyl groups, was not used and the polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, was taken in 100 parts by mass. Characteristics thereof are shown in Table 1.

[0044]

Example 3.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting replacement of the resin mixture in Example 1 with the mixture of 50 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the

hydrogen atoms by 1-ethoxyethyl groups, and 50 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 30% by moles of the hydroxyl groups were substituted for the hydrogen atoms by tetrahydropyranyl groups. Characteristics thereof are shown in Table 1.

[0045]

#### Example 4

A positive-working resist composition was prepared in the same manner as in Example 1 excepting the replacement of the resin mixture in Example 1 with the mixture of 60 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 39% by moles of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, and 40 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a molecular weight dispersion of 1.2, of which 30% by moles of the hydroxyl groups were substituted for the hydrogen atoms by *tert*-butyl groups. Characteristics thereof are shown in Table 1.

[0046]

#### Example 5.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting the replacement of the resin mixture in Example 1 with the mixture of 60 parts by mass of a copolymer having a mass-average molecular weight of 10000 and consisting of 65% by moles of hydroxystyrene, 20% by moles of styrene and 15% by moles of *tert*-butyl acrylate and 40 parts by mass of a copolymer having a mass-average molecular weight of 10000 and consisting of 75% by moles of hydroxystyrene, 20% by moles of styrene and 5% by moles of *tert*-butyl acrylate. Characteristics thereof are shown in Table 1.

[0047]

#### Comparative Example 1.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, salicylic acid was not used. Properties thereof are shown in Table 1.

[0048]

Comparative Example 2.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, triethylamine was not used. Properties thereof are shown in Table 1.

[0049]

Comparative Example 3.

A positive-working resist composition was prepared in the same manner as in Example 2 except that, in Example 2, salicylic acid was not used. Properties thereof are shown in Table 1.

[0050]

Comparative Example 4.

A positive-working resist composition was prepared in the same manner as in Example 2 except that, in Example 2, triethylamine was not used. Properties thereof are shown in Table 1.

[0051]

Comparative Example 5.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, 1,4-cyclohexane dimethanol divinyl ether was not used. Properties thereof are shown in Table 1.

[0052]

[Table 1]

		Sensitivity (mJ/cm <sup>2</sup> )		Profile of resist pattern		Resolu- tion ( $\mu$ m)		Thermal flow charac- teris- tics
		(1)	(1')	(2)	(2')	(3)	(3')	
Exam- ple	1	45	45	rectangular	rectangular	0.19	0.19	⊙
	2	47	47	rectangular	rectangular	0.18	0.18	○
	3	45	45	rectangular	rectangular	0.19	0.19	⊙
	4	45	45	rectangular	rectangular	0.20	0.20	⊙
	5	25	25	rectangular	rectangular	0.19	0.19	⊙
Com- para- tive Exam- ple	1	30	35	inversely tapered form	inversely tapered form	0.24	0.24	○
	2	20	33	trapezoidal form	trapezoidal form	0.25	0.25	○
	3	20	20	inversely tapered form	inversely tapered form	0.23	0.23	×
	4	18	28	trapezoidal form	trapezoidal form	0.23	0.23	×
	5	35	35	rectangular	rectangular	0.20	0.21	△

[0053]

(1) and (1'), (2) and (2') and (3) and (3') in the table show the results of the twice repetition of the same measurements.

[Name of document] Abstract

[Abstract]

[Problems] Provided is a positive-working resist composition having good stability in the lapse of time and capable of giving a patterned resist having excellent pattern resolution and resistance against etching with a small amount of dimensional change per unit temperature by the thermal flow process.

[Means for solution] A positive-working resist composition is to contain (A) a resinous base ingredient consisting of at least one kind of hydroxystyrene-based copolymers of which at least a part of the phenolic hydroxyl groups or carboxyl groups are substituted for the hydrogen atoms thereof by acid-dissociable groups; (B) a compound generating an acid by irradiation with a radiation; (C) a divinyl ether compound having crosslinkability; (D) an organic carboxylic acid consisting of atoms of carbon, oxygen and hydrogen alone; and (E) an organic amine.

[Figure selected] None

INFORMATION OF RECORD OF APPLICANT

Identification number                   〔000220239〕

1. Date of change	30th August 1990
[Reason of change]	Newly registered
Address	150, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken
Name	TOKYO OHKA KOGYO CO., LTD.